Experimental Report

Proposal: **5-24-511** **Council:** 4/2012

Title: Size-dependent crystal structure and phase transitions in ZrO2-Sc2O3 nanomaterials for intermediate-temperature solid-oxide fuel cells

This proposal is a new proposal

Researh Area: Materials

Main proposer: **LAMAS Diego German**

Experimental Team: CRAIEVICH ALDO
LAMAS Diego German
ABDALA Paula Macarena

Local Contact: CUELLO Gabriel Julio

Samples: ZrO2-X mol% Sc2O3 nanopowders, 2 < X < 14, average crystallite sizes of about 20-25 nm (13 samples)
ZrO2-8 and 12 mol % Y2O3 powders, as reference materials (2 samples)
Pure (undoped) ZrO2 nanopowders, average crystallite sizes between 5 and 40 nm (4 samples)

Instrument	Req. Days	All. Days	From	To
D1B	3	3	26/11/2012	29/11/2012

Abstract:

Because of their excellent ionic conductivity, the highest among all ZrO2-based materials, ZrO2-Sc2O3 ceramics have attracted great attention. They are considered promising candidates for solid electrolytes in intermediate temperature solid-oxide fuel cells. However, for T<600°C, they exhibits low-conductivity rhombohedral phases that affect their performance. In previous works, we demonstrated that these phases of poor properties can be avoided in nanomaterials.

In this proposal, we plan to investigate by ND the crystal structure at room temperature of tetragonal (t',t'') or cubic ZrO2-2 to 14 mol% Sc2O3 nanopowders with crystallite sizes of 20-25 nm, in order to analyze the O2- sublattice and determine the displacement of O2- anions from their ideal positions in the fluorite-like cubic phase. We are particularly interested in the case of the t''-form of the tetragonal phase, with exhibits a c/a ratio of unity. For selected compositions, we also plan to perform high-temperature ND studies in order to monitor the O2- sublattice in the t' --> t'' and t'' --> cubic transitions. In addition, pure ZrO2 nanopowders and ZrO2-Y2O3 solid solutions will be analyzed as reference materials.

Size-dependent crystal structure and phase transitions in ZrO_2-Sc_2O_3 nanomaterials for intermediate-temperature solid-oxide fuel cells

Introduction and scientific background

ZrO_2-Sc_2O_3 ceramics have attracted great attention because they are promising candidates for solid electrolytes used in intermediate-temperature solid-oxide fuel cells. At high temperatures ZrO_2-Sc_2O_3 ceramics exhibit excellent ionic conductivity, the highest among all ZrO_2-based materials. However, for classic ceramics (with micrometer sized crystallites), the high-conductivity cubic phase is only stable at temperatures above 600°C, while at lower temperatures the stable phases are rhombohedral, these phases exhibiting poor electrical properties. The cubic-rhombohedral transition, on cooling, causes the degradation of the electrical and mechanical properties of this material. From a technological point of view this is a key problem and, therefore, the equilibrium phase diagram of the ZrO_2-Sc_2O_3 system has been thoroughly studied by many authors. Although substantial progress has been made in recent years, many uncertainties still remain.

Depending on composition and temperature, bulk ZrO_2-Sc_2O_3 exhibits monoclinic, tetragonal, cubic, or rhombohedral (β, γ, and δ) phases [1]. The tetragonal and cubic phases have excellent electrical properties, whereas the performance of the monoclinic and rhombohedral phases is poor. The phase diagram of ZrO_2-Sc_2O_3 proposed by Ruh *et al.* [2] is widely accepted, even though some details are still under discussion.

In compositionally homogeneous ZrO_2-based solid solutions, the tetragonal phase, for different compositions, exhibit three forms, known as t, t', and t" [1]. The stable tetragonal form is called the t-form. The t′-form has a wider solubility but is unstable in comparison with the mixture of t-form and cubic phase. Finally, the t"-form has an axial ratio, *c/a*, of unity, with the oxygen atoms displaced along the c-axis from their ideal sites of the cubic phase. In most of ZrO_2-based systems, as the dopant content increases, the tetragonal structure gradually changes to the cubic one, exhibiting t' --> t" and t" --> cubic transitions. However, Yashima and co-workers proposed a metastable phase diagram for compositionally homogeneous ZrO_2-Sc_2O_3 materials of large average crystallite sizes without the presence of the metastable t"-form [1,3]. These authors concluded that, for solid solutions with Sc_2O_3 contents between 10 and 12 mol%, the rhombohedral β phase coexists with the cubic one [1,3]. The retention of the t"-form in ZrO_2-Sc_2O_3 has been firstly reported by Xu *et al.* for nanopowders synthesized by a hydrothermal process [4]. Since these authors identified the t"-form by using Raman spectroscopy, our research group conducted a detailed crystallographic study of nanocrystalline and compositionally homogeneous ZrO_2-Sc_2O_3 solid solutions by synchrotron using X-ray powder diffraction (SXPD) and analysed the influence of crystallite size on the equilibrium phase diagram of this system.

We have studied the crystal structure, phase transitions and local atomic order of compositionally homogeneous ZrO_2-Sc_2O_3 solid solutions with Sc_2O_3 content between 1 and 14 mol% and average crystallite sizes between 10 and 100 nm by SXPD, Raman spectroscopy and EXAFS spectroscopy [5-9]. Our results demonstrated that these nanomaterials with average crystallite sizes (D) under 35 nm, at room temperature, exhibit a single cubic or tetragonal phase over the whole compositional range [6]. On the contrary, samples with Sc_2O_3 contents between 10 and 14 mol% with larger crystallite sizes (D > 35 nm) exhibit a mixture of a cubic (or tetragonal t") phase at room temperature coexisting with different rhombohedral phases (β and γ), the content of these rhombohedral phases increasing for increasing average sizes [7]. We also investigated the phase transitions as function of temperature in these materials, in order to analyze the influence of the crystallite size on the ZrO_2-Sc_2O_3 phase diagram, finding strong changes when comparing nanopowders and conventional microcrystalline samples [6,7,9]. The absence of the low-conductivity phases in nanomaterials is very important from a technological point of view.

All these previous studies were performed by SXPD. Even though a high-intensity configuration allowed us to detect small Bragg peaks related to O^{2-} anion displacements, neutron diffraction (ND)

experiments provide a more precise analysis of the O^{2-} sublattice. This is expected to occur because the atomic scattering factor of oxygen for neutrons is much higher than that associated to X-rays. In fact, ND has proved to be an excellent technique for the analysis of O^{2-}-ionic conductors [10] and it has been used for the determination of the crystal structure of complex rhombohedral phases [5].

Experimental procedure

We have investigated the crystal structure of ZrO_2-0 to 13 mol% Sc_2O_3 nanopowders by ND using the D1B instrument. We analyzed the O^{2-} sublattice and determined the displacement of O^{2-} anions from their ideal positions in the cubic phase. In particular, we studied the case of the t''-form of the tetragonal phase, with exhibits a ratio *c/a=1*. These samples were synthesized by a nitrate-lysine gel-combustion route [6]. Two calcination temperatures, 600 and 800°C, were selected in order to get average crystallite sizes of about 10 and 25 nm, respectively. For a few compositions (8, 10 and 11 mol% Sc_2O_3), we also performed high-temperature ND measurements, up to 800°C, in order to monitor the O^{2-} sublattice in the t' --> t'' and t'' --> cubic phase transitions. The wavelength was of 1.869 Å. Additional experiments at room temperature were conducted in the D20 instrument.

In addition to ND experiments, SXPD measurements were conducted at the BM01-A beamline, Swiss-Norwegian Beamlines at European Synchrotron Radiation Facility (ESRF, Grenoble, France). The X-ray wavelength was selected to be 0.6941 Å and a Pilatus 6M detector was used. These SXPD measurements allowed us to determine the lattice parameters and axial ratio with high precision, thus allowing us to safely identify the tetragonal forms.

Preliminary results

Figure 1 exhibits the ND patterns corresponding to ZrO_2-6 to 13 mol% Sc_2O_3 nanopowders calcined at 600 and 800°C, measured with D1B and D20 instruments, respectively. By following the region close to the 112 Bragg peak of the tetragonal structure, it can be observed that its intensity decreases with increasing Sc_2O_3 content, indicating that the tetragonal phase transforms to the cubic phase. The t''/cubic compositional boundary is located between 11 and 13 mol% Sc_2O_3, in agreement with our previous studies [3].

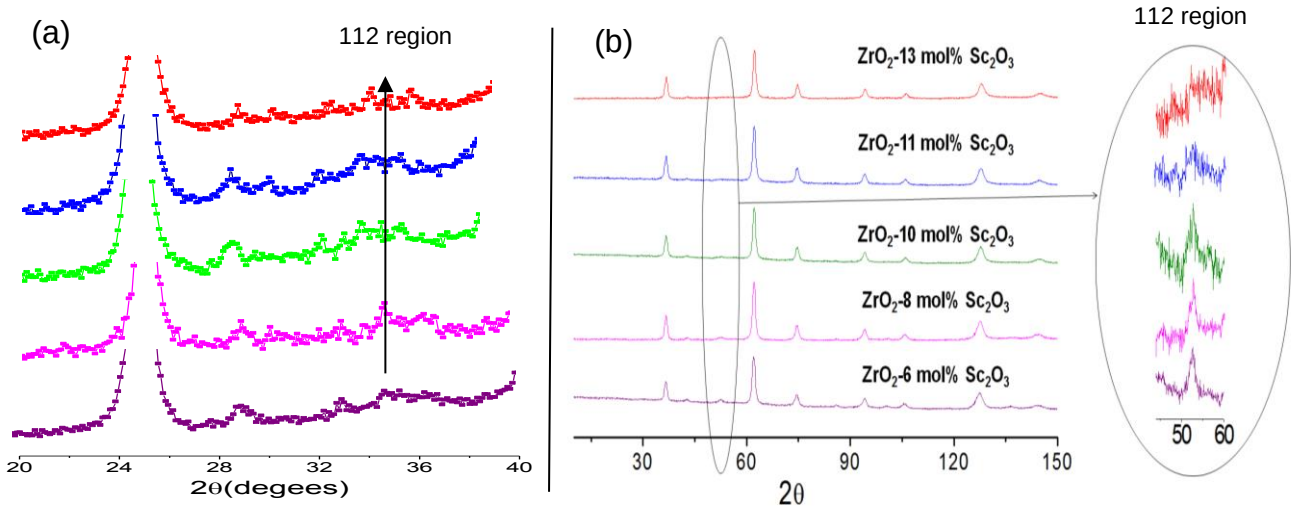

Figure 1: a) ND patterns for ZrO_2-6, 8, 10, 11 and 13 mol% Sc_2O_3 nanopowders calcined at 600°C, collected with 1B instrument. b) ND patterns for ZrO_2-Sc_2O_3 nanopowders calcined at 800°C, collected with D20 instrument (data zoom in the region of the 112 peak).

ND data had not enough 2θ resolution to discriminate between the t' and t'' forms because the axial ratio of the t'-form is very close to unity. For this reason, SXPD measurements were also performed. Combined Rietveld refinements of ND and SXPD data allowed us to obtain precise results of both the axial ratio and the O^{2-}-ion displacement. For example, Figure 2 displays the refinements

corresponding to the ZrO_2-6 mol% Sc_2O_3 sample, which exhibited the t'-form: a = 5.08599 (2) Å, c = 5.1386 (2) Å, z(O) = 0.2101 (2). Similar analysis on the ZrO_2-10 mol%Sc_2O_3 nanopowder confirmed that this sample exhibits the t''-form: *a* = *c* = 5.0875 (5) Å, *z*(O) = 0.2263 (5). These results are in agreement with those of our previous studies [5-9], but the use of ND allowed us, as expected, to determine the oxygen displacements with higher precision than with SXPD.

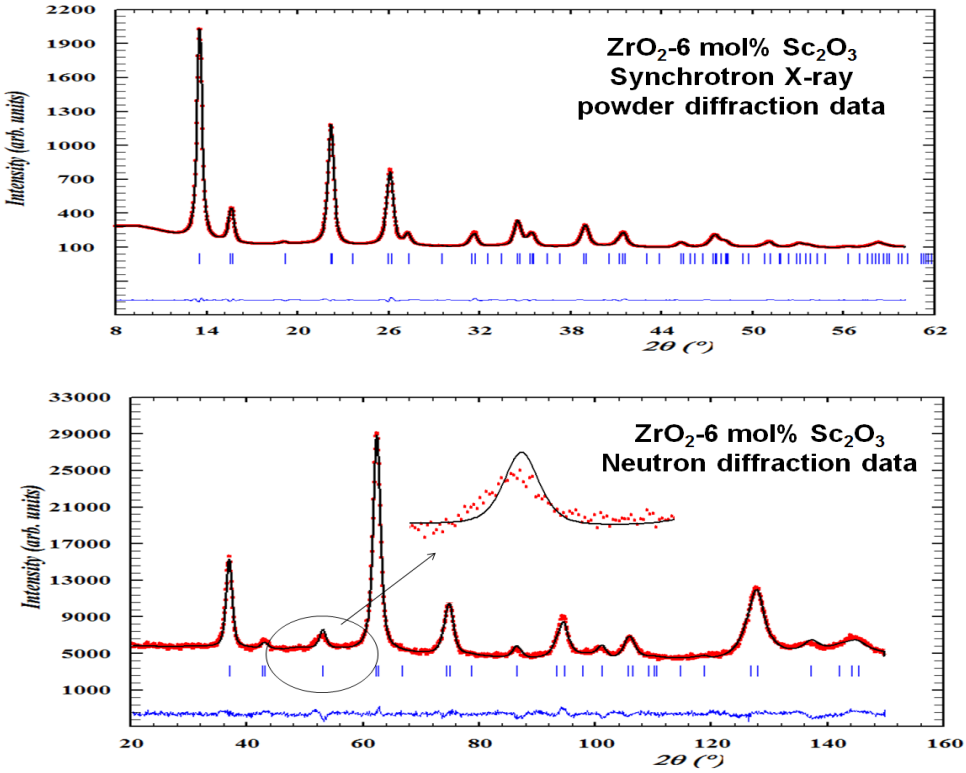

Figure 2: Combined Rietveld refinements of ND and SPXD data for ZrO_2-6 mol% Sc_2O_3 nanopowder

Conclusions

Combined neutron and synchrotron X-ray powder diffraction analyses allowed us to obtain precise determinations of the lattice parameters and O^{2-} anion displacements in ZrO_2-Sc_2O_3 solid solutions.

The first results presented here confirmed the main conclusions of our previous works [5-9], particularly those related to the existence of the tetragonal t''-form, with axial ratio (*c/a*) of unity, but with O^{2-} anions displaced from their positions in the cubic phase along the c-axis [6,7,9].

By taking advantage of the high scattering factor of oxygen atoms for ND, we have determined the O^{2-} displacements with a precision higher than in our previous studies by SXPD.

References

1. M. Yashima, M. Kakihana, M. Yoshimura, *Solid State Ionics* **86-88** (1996) 1131
2. R. Ruh, H.J. Garrett, R.F. Domagala, V.A. Patel, *J. Am. Ceram. Soc.* **60** (1977) 399
3. H. Fujimori, M. Yashima, M. Kakihana, *J. Am. Ceram. Soc.* **81** (1998) 2885
4. G. Xu, Y.W. Zhang, C.S. Liao, C.H. Yan, *Phys. Chem. Chem. Phys.* **6** (2004) 5410
5. P.M. Abdala, D.G. Lamas, M.E. Fernández de Rapp, N.E. Walsöe de Reca, A.F. Craievich, M.C.A. Fantini, *Powder Diffraction* **23** (2008) S87
6. P.M. Abdala, A.F. Craievich, M.C.A. Fantini, M.L.A. Temperini, D.G. Lamas, *J. Phys. Chem. C* **113** (2009) 18661
7. P.M. Abdala, M.C.A. Fantini, A.F. Craievich, D.G. Lamas, *Phys. Chem. Chem. Phys.* **12** (2010) 2822
8. P.M. Abdala, D.G. Lamas, M.C.A. Fantini, A.F. Craievich, *J. Alloy Compnds.* **495** (2010) 561
9. P.M. Abdala, Ph.D. Thesis, Universidad de Gral. San Martín, San Martín, Argentina (2010)
10. J.A. Alonso, M.J. Martínez-Lope, A. Aguadero, L. Daza, *Prog. Solid State Chem.* **36** (2007) 134